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# David W. Taylor Naval Ship Research and Development Center

Bethesda, MD 20084-5000

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DTRC/SME-88/08 April 1988

Ship Materials Engineering Department  
Research and Development Report

A STUDY OF VARIABLES AFFECTING RESULTS IN THE D2274  
ACCELERATED STABILITY TEST

Part 2 - Effects of Selected Chemical Variables

by

Dr. E.W. White

DTRC/SME-88/08 A Study of Variables Affecting Results in the D2274  
Accelerated Stability Test  
Part 2 - Effects of Selected Chemical Variables



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			Navy Fuel	Fuel Stability	Oxygen Content
			Diesel Fuel	ASTM D2274	Metals Effect
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>Different laboratories have been unable to obtain comparable stability results on a fuel sample when the ASTM D2274 test procedure has been used. This Center is attempting to identify critical variables that cause inconsistencies. Five chemical variables were examined that included: oxygen purity, residual acidity, metallic contacts, copper concentrations, and exposure to ultraviolet light.</p> <p>Experiments with nitrogen, air, and oxygen show that insolubles increase with oxygen concentration. Other experiments show that acidity, iron oxide, iron-copper coils, ultraviolet radiation, and increasing levels of cupric acetyl acetonate yield increasing amounts of insolubles.</p> <p>The general conclusion is that the samples should not be shipped in contact with metallic or rusty cans; they should not be exposed to light during sampling, shipping,</p>					
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Acidity Ultraviolet Radiation

Block 19 (Continued)

For laboratory testing; and they should not contact copper-containing metals. Further, laboratory personnel should ensure that all traces of acidic cleaning compounds are removed from glassware and that only high purity oxygen is used. *Handwritten: No. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 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# ABBREVIATIONS

°API	Gravity by American Petroleum Institute scale
ASTM	American Society for Testing and Materials
°C	Degrees Celsius
cm	Centimeters
cSt	Centistokes
Cu	Copper
DMP	Dimethylpyrrole
°F	Degrees Fahrenheit
FIA	Fluorescent indicator adsorption
GC	Gas chromatography
HPLC	High-pressure liquid chromatography
Hz	Hertz
LCO	Light cycle oils
L/hr	Liters per hour
M	Molar
μm	Micrometers
mg KOH/g	Milligrams of potassium hydroxide per gram
mg/mL	Milligrams per milliliter
mL	Milliliters
mm	Millimeters
NDF	Naval Distillate Fuel
NTP	Normal temperatures and pressure
OD	Outside diameter
pKa	Negative logarithm of dissociation constant
ppm	Parts per million

SD	Standard deviation
SR	Straight run
SWRI	Southwest Research Institute
TAN	Total acid number
UV	Ultraviolet
wt	Weight

## ABSTRACT

Different laboratories have been unable to obtain comparable stability results on a fuel sample when the ASTM D2274 test procedure has been used. This Center is attempting to identify critical variables that cause inconsistencies. Five chemical variables were examined that included: oxygen purity, residual acidity, metallic contacts, copper concentrations, and exposure to ultraviolet light.

Experiments with nitrogen, air, and oxygen show that insolubles increase with oxygen concentration. Other experiments show that acidity, iron oxide, iron-copper coils, ultraviolet radiation, and increasing levels of cupric acetyl acetonate yield increasing amounts of insolubles.

The general conclusion is that the samples should not be shipped in contact with metallic or rusty cans; they should not be exposed to light during sampling, shipping, or laboratory testing; and they should not contact copper-containing metals. Further, laboratory personnel should ensure that all traces of acidic cleaning compounds are removed from glassware and that only high purity oxygen is used.

## ADMINISTRATIVE INFORMATION

The work described in this report was conducted as part of the Navy Energy Program over a period of 3 years. Preliminary testing began in 1982, but the first major block of work was initiated in January 1983.

The work was funded by the Naval Material Command, Code 08E (Dr. Alan Roberts and Mr. Wayne Vreath), under Program Element 63724N, and Task Area R0838. The program was block-funded to this Center with Dr. C.F. Krolick (Code 275) as the Block Program Manager and Mr. Richard Strucko (Code 2759) as the Project Engineer.

The Center's laboratory work was conducted by Code 2832 personnel with Dr. Edmund White as the Technical Manager. The work was performed under Center Work Units 2759-172 in FY 1983, 2759-212 in FY 1984, 2759-313 in FY 1985.

## INTRODUCTION

Different laboratories have been unable to obtain the same results when determining the stability of identical samples of middle distillate fuels by the ASTM D2274 Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method). Government, industry, and other interested groups are concerned about the lack of a method with good reproducibility to evaluate the stability of fuels.

Despite its poor reproducibility and the tenuous relationship of its results to the real world, the ASTM D2274 method has provided a means to keep unstable fuel out of the Navy's fuel system. However, in late 1980, the Navy encountered a fuel that had passed the limitations of ASTM D2274 for total insolubles, and still produced plugged filters and nozzles during ship use. (The Navy specification for Naval Distillate Fuel (MIL-F-16884) limited the total insolubles measured by the method to a maximum of 2.5 mg/100 mL). Apparently, the D2274 procedure was no longer able to keep unstable fuel out of the Navy fuel system, possibly as a result of the changing nature of fuels available to the Navy.

As a direct consequence of this problem, the maximum level of D2274 total insolubles permitted by the specification was reduced to 1.5 mg/100 mL of fuel. This Center initiated a program to develop an improved accelerated stability test. The first step was to conduct an experimental evaluation of the variables that we thought affected the results obtained with the D2274 procedure. We surmised that poor control of critical variables may explain the poor reproducibility between laboratories.

Some of the results of our variable study were reported previously.<sup>1,2</sup> An ASTM survey revealed that there were wide variations in practice for most steps in the procedure among those using the method. We also found wide variations in the results obtained by five different analysts in our laboratory. These facts supported the assumption that poor control of critical variables may provide an explanation.

We also found that the temperature, time in bath, and oxygen flow rate called for in the method, are not major considerations if kept within the specified limits.

This report examines five factors of a chemical nature that could affect the reproducibility problem.

1. Oxygen purity because oxygen is a reactant.
2. Acid residue because the use of chromic acid to clean glassware is part of the ASTM D2274 method.
3. Iron oxide contamination resulting from the sample collection containers.
4. Metallic copper contamination because of previous implication in the oxidation of fuels.
5. Ultraviolet (UV) radiation exposure because it is suspected to be a chain initiator in the fuel oxidation process.

The results obtained from experiments conducted to test these hypotheses are presented.

## TECHNICAL BACKGROUND

### FUEL STABILITY TESTS

All liquid, petroleum-derived fuels tend to form gums and sediments when stored in contact with air. However, the number and concentration of reactant species varies from fuel to fuel; as a result, the quantities and rates of formation of such gums and sediments vary also. Because the mechanisms of formation are poorly understood, we simulate storage and measure the adherent insolubles (gums) and the filterable insolubles (sediments), rather than predict the stability of a fuel from its chemical analysis.

To speed up reaction rates, tests simulating liquid fuel storage deviate from real-world conditions by aging the test fuel at temperatures above ambient. The reaction rate is defined by the Arrhenius equation and ranges from about 1.7 to 3 times greater per 10°C increase in temperature.<sup>3,4</sup>

Tests that simulate storage serve two basic purposes, research and quality control. As a research tool, the newly standardized ASTM D4625 Test Method for Distillate Fuel Storage Stability at 43°C (110°F) is such a method. Its relatively low temperature represents only a small rise from ambient conditions, so the relative importance of the various reactions that create gums and sediments are not changed appreciably.

Personnel at the Bureau of Mines Experiment Station,\* Bartlesville, Oklahoma, conducted work in the 1950's on 34 mid-distillate fuels and 250 blends. Results showed that bottle storage at 43°C for 13 weeks was essentially equivalent to drum storage at ambient temperature for a year.<sup>5</sup> Subsequent studies conducted at this Center and reported by Garner and White,<sup>6</sup> who tested heavier distillates, showed a similar result; i.e., 1 week of storage at 43°C produced as much total insolubles as a month of storage under the outdoor ambient temperatures prevalent in Annapolis, Maryland.

The second type of test is used for quality control in the production or purchase of fuel. This type of test must be completed quickly, within approximately 24 hr. Test temperatures must be appreciably higher than ambient to attain the rapid aging of the test fuel. ASTM D2274 Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method) uses a temperature of 95°C and pure oxygen vis-a-vis air to complete aging in 16 hr. Unfortunately, the 70°C increase in

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\*The Bureau of Mines Experiment Station has evolved over the years into what is now known as the National Institute for Petroleum and Energy Research.

temperature over ambient, which should increase reaction rates about 128 times, also may lead to a confounding of relationships among the many reactions that occur. Such a possibility must be recognized in using the test.

In brief, the D2274 procedure consists of aging 350 mL of filtered fuel at 95°C (203°F) for 16 hr, while oxygen is bubbled through the fuel at a rate of 3 L/hr. Following the aging stage, the fuel is cooled to ambient temperature (22° to 27°C (72° to 80°F)), in the dark, before it is filtered, to recover the filterable insolubles. Insolubles adhering to the glassware are recovered by rinsing with a solvent consisting of equal volumes of benzene, acetone, and methanol. (Toluene is now usually substituted for benzene for safety considerations.) The solvent is evaporated, and the residual adherent insolubles are weighed. The sum of the filterable and adherent insolubles is reported as the total insolubles.

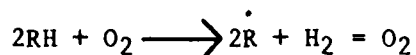
#### STABILITY REACTIONS

The formation of gums and sediments in fuels has long been recognized as a result of oxidation and subsequent reactions. In 1958, Sauer, et al,<sup>7</sup> proposed a mechanism for organic sediment formation in heating oils that consisted of:

- The side chain oxidation of reactive compounds in the fuel to form hydroperoxides.
- The partial decomposition of the hydroperoxides by the splitting out of water to form aldehydes.
- The reaction of the aldehydes with other peroxides to form peroxyhemiacetals.
- The decomposition of the peroxyhemiacetals to form monomeric oxidation products by one path, and condensed, esterified products of higher molecular weight by another path.

Experimental evidence that oxygen from the air does indeed react with reactive components of a fuel appears throughout the literature. In a study of the oxidation of pyrrole and picolines (two nitrogen-containing compounds that could be present in fuels), Bartok, et al,<sup>8</sup> noted an oxygen absorption related to the moles of the organic compound. Mayo and Lan<sup>9</sup> found a correspondence between the rates of oxygen absorption and the rates of gum formation in a series of oxidations at 130°C under air. Yaggi, et al,<sup>10</sup> reported oxygen absorption is higher with coal liquids than with upgraded coal liquids which are comparable to petroleum jet fuel in oxygen absorption. Cooney and Wechter<sup>11</sup> found that 2,5-dimethyl pyrrole in a shale-derived diesel fuel decreased in proportion to the oxygen uptake by the fuel. Hazlett, et al,<sup>12</sup> found variations in the peroxide numbers of jet fuels with time, and related the peroxide number to the formation of hydroperoxides. The curves of peroxide number as a function of time are reminiscent of the concentration of the intermediate species in the classical series reaction.

Generally, it is assumed that a free radical, chain mechanism is involved. Taylor and Frankenfeld<sup>13</sup> indicated a simplified mechanism in which a free radical is formed from the organic compound; oxygen is added to the free radical to yield an oxygenated free radical, which can propagate other basic free radicals by reaction with other molecules of the organic compound; and the chain is terminated by the reaction of several molecules of the oxygenated free radical to form inert materials. Betts and Uri<sup>14</sup> had pointed out the possibility of a termolecular initiation step:



Beaver, et al,<sup>15</sup> recently proposed that the first step of the oxidation of alkylpyrroles involves the reversible formation of a molecular association complex between the alkylpyrrole and dissolved oxygen. Different reactions proceeding by

different mechanisms are possible, because of the large number of reactive compounds that can be present in a fuel. This complexity leads us to question accelerated stability tests that deviate greatly from ambient temperatures.

#### OXYGEN ADDITION STEP

Regardless of the exact mechanism of insolubles formation, oxygen is one of the reactants in some sort of a bimolecular reaction step. Moreover, since the reaction is taking place in solution in the fuel, it is not the concentration of oxygen in the gas phase but rather that which is dissolved in the fuel that is important. Further, since dissolved oxygen is being depleted in the instability reactions, an equilibrium concentration will be established resulting from the rate of replenishment from the gas phase and that of consumption.

In the D2274 procedure, a supply of oxygen is introduced through 7-mm-diameter glass tubing near the bottom of a 350-mL volume of fuel. Bubbles of oxygen rise through about 340 mm of fuel. The bubbles provide a source of oxygen and agitate the body of the liquid through the movement of liquid carried along by the bubbles.

We may assume that oxygen moves by diffusion from the gas bubbles into the liquid fuel in accordance with Fick's Law. The oxygen that diffuses from the bubble into the liquid depends upon the diffusion coefficient, the surface area of the bubble, and the concentration gradient between the oxygen in the bubble and the oxygen concentration in the liquid.

We also may assume that a relatively quiescent boundary layer of liquid surrounds the bubble of gas. Sherwood's description<sup>16</sup> of gaseous absorption, followed by a rapid irreversible reaction in the liquid phase, predicts that the zone of reaction between the oxygen and the reactive components in the liquid quickly moves away from the gas-liquid interface to an equilibrium position in the boundary layer. Thus, equilibrium position becomes the site where oxygen diffusing

into the system from the gas bubble meets reactive fuel components diffusing to the reaction site from the body of the fuel. Depending on the relative speeds of reaction, intermediate products such as the postulated hydroperoxides may diffuse to the body of the liquid before reacting further to form insolubles, or they may react at or near their site of formation.

The D2274 process is far more complex than Sherwood describes. The boundary layer around a bubble exists for only a short time between the time the bubble forms and the time it reaches the surface of the liquid and escapes to the gas phase above the liquid. Thereupon, the boundary material now separated from its gaseous companion becomes once more part of the body of fuel liquid.

The pressure of oxygen in a bubble at its formation is approximately atmospheric plus that equivalent to about 340 mm of fuel (about 22 mm Hg or 0.027 atm). If there were no chemical reaction, the concentration of oxygen in the fuel in equilibrium at this pressure is about 0.18 liter per liter of fuel, corrected to an NTP of 0°C and 1 atm (according to ASTM D3827-83, Estimation of Solubility of Gases in Petroleum and Other Organic Liquids). As a first approximation, the concentration of oxygen in equilibrium with air, instead of pure oxygen, at 1 atmosphere pressure would be about one-fifth of this value.

We would expect no formation of insolubles from oxidative reactions, with pure nitrogen as the gas rather than oxygen. In fact, the flow of nitrogen could be expected to strip dissolved oxygen out of the system. Any insolubles formed would have to result from nonoxidative reactions, such as the polymerization of olefinic compounds or from precursors such as hydroperoxides formed in the fuel prior to the test.

## EFFECT OF ACIDITY

ASTM D2274-74 specified the cleaning of oxygen delivery tubes, containers, and new oxidation cells with chromic acid. Since some organic reactions can take place in acid but not in alkaline conditions, and vice versa, failure to remove chromic acid fully during the subsequent rinsing could change the results in the stability test.

Recent stability research work has resulted in a number of papers being written on the effects of various acidic substances. In 1981, Frankenfeld and Taylor<sup>17,18</sup> reported that organic acids (especially n-decanoic acid) have strong accelerating effects on sediment formed from 2,5-dimethylpyrrole (DMP), in n-decane as diluent, but appeared to have little effect in fuels. A series of tests designed to resolve this ambiguity, found that while decanoic acid augmented sediment formation from DMP in decane or in JP-8, it had little effect in diesel fuel which already had an appreciable acid titer.

Daniel<sup>19</sup> reported a relationship between the acidity/basicity expressed as pKa of a series of indoles, pyridines, and quinolines, and the logarithm of the deposit in a diesel fuel.

Cooney, et al,<sup>20</sup> reported examining the effects of 10 organic acids and bases when used as co-dopants in a shale-derived diesel fuel. The 10 compounds were acetic acid, hexanoic acid, decanoic acid, p-toluenesulfonic acid, dodecylbenzene sulfonic acid, nicotinic acid, 3-pyridinesulfonic acid, tri-n-butylamine, N,N'-dimethylaniline, and 4-dimethylaminopyridine. The first three compounds (the carboxylic acids) all interacted synergistically with DMP-doped fuel. Mixed results ranging from a strong positive to a strong negative were obtained with the sulfonic acids. The 4-dimethylaminopyridine always reacted in a strong positive manner with the DMP-doped fuel, but the other base items seemed to have little effect. Similar results were obtained when the dopant was 3-methylindole rather than DMP.

At the Second International Conference on Long-Term Storage Stabilities of Liquid Fuels, Hazlett and Kelso<sup>21</sup> reported that carboxylic and organic sulfonic acids increased deposit formation when added to distillate fuel blends containing catalytically cracked stock. They also showed that the carboxylic acids data fitted a unified treatment based on hydrogen ion concentration calculated from pKa values for aqueous solutions. Further, they found that the action of a tertiary aliphatic amine stabilizer could be explained as that of counteracting strong acids in the fuels.

At the April 1987 meeting of the American Chemical Society, Beal, et al,<sup>22</sup> reported on further studies with a shale-derived diesel fuel. They used two organic acids (hexanoic acid and dodecylbenzene sulfonic acid) and two bases (tri-n-butylamine and 4-dimethylaminopyridine) as co-dopants with 2-methylpyridine, 2,6-dimethylquinoline, or dodecahydrocarbazole in the shale fuel. The acids and bases were used at a concentration of  $3.21 \times 10^{-2}$  M. They reported that, with the 2-methylpyridine doped fuel, only the sulfonic acid exhibited a very strong interaction (i.e., a much higher level of total insolubles). In fuels doped with 2,6-dimethylquinoline, the sulfonic acid causes a copious amount of a tan solid to form, a material that was postulated to be sulfonic acid salt. In fuels doped with dodecahydrocarbazole, the two acids suppressed the formation of insolubles; whereas, the tri-n-butylamine resulted in more insolubles.

In general, the acidity/basicity of the fuel seems important, but the effects are variable and depend on other substances in the fuel. This represents an area that needs further study.

## EFFECT OF METAL AND METAL COMPOUNDS

There is a whole body of literature on metals and metallic compounds as catalysts for the oxidation of organic compounds. Only a few of the references on the interaction between metals or metallic compounds and petroleum products are discussed below.

In 1952, Sawyer<sup>23</sup> reported that the use of copper and low-carbon steel in lubricating oil systems has an adverse effect on the properties of the oils. In 1964, Wilson<sup>24</sup> reported that some turbine oils are susceptible to soluble copper catalysis, some to metallic copper catalysis, and some to both forms of catalysis. In 1977, Stavinocha and La Pera<sup>25</sup> reviewed diesel fuel deterioration and reported that trace amounts of metals such as copper, cobalt, lead, zinc, and iron can contribute to deterioration during storage.

More recently, Frankenfeld and Taylor<sup>26</sup> indicated that copper, vanadium alloys, and iron are active catalysts. However, their experiments with copper, steel, and tin-coated steel stored for 7 and 14 days at 43°C (110°F) showed a slight decrease in sediment in the presence of the metals. Daniel<sup>27</sup> reported in 1983 that the amount of increased deposits is a function of the surface area of copper foil present in a Jet A fuel during a 121°C (250°F)/168 hr exposure. In a test under identical conditions with copper (II) acetylacetonate rather than copper strips, he found that the amount of deposit is a linear function of the amount of the copper compound used.

## EFFECT OF ULTRAVIOLET RADIATION

The rapid darkening of a distillate fuel sample upon exposure to sunlight is a common experience among petroleum chemists, and is a visual manifestation of a reaction initiated by the absorption of visible light to form an excited species. The Stark-Einstein Law of the Photochemical Equivalent postulates that each molecule

taking part in a chemical reaction induced by exposure to light absorbs one quantum of the radiation causing the reaction.<sup>28</sup> Glasstone, et al,<sup>29</sup> postulates that a dissociation to atoms or radicals occurs following the raising of a molecule to a higher energy level by absorption of light energy. These radicals then undergo reactions determined by thermal considerations. In brief, the absorption of light is the chain initiator in an oxidative or other type of reaction.

Frankenfeld and Taylor<sup>26</sup> reported that the formation of fuel sediments in the dark is always a linear function of time; whereas, similar reactions while the fuel is exposed to light are sharply curved above the trend line for oxidation in the dark. Their plotted data indicate that similar results are obtained with sunlight and with ultraviolet light.

## DESCRIPTION OF EQUIPMENT AND MATERIALS

### GENERAL INFORMATION

All tests were conducted in apparatus designed for the ASTM D2274 test procedure. Solvents used in that test were reagent grade except for the hydrocarbon solvent which was knock-engine grade, as specified in ASTM D2274. Only one operator or team was used within each individual study so that operator bias would not be a factor in the study of any one chemical effect. An earlier study<sup>2</sup> showed that different operators could obtain different results on the same sample in the same laboratory.

### APPARATUS

All tests were conducted in an eight-cell oxidation apparatus manufactured by Lawler Manufacturing, Inc., for use in the D2274 stability test. The apparatus draws 9 amperes from a 115-volt, 60-Hz power supply.

In tests where the fuels were exposed to ultraviolet radiation, the ultraviolet lamp used in conjunction with the fluorescent indicator adsorption test (ASTM D1319) was employed. It was placed approximately 12 in. from the fuel, which had been filtered and placed in an oxidation cell.

#### MATERIALS

Studies of specific chemical effects were conducted on one, two, or three fuels depending upon the specific study. These fuels were the same ones used in earlier work.<sup>1,2</sup> While all were diesel-range fuels, they came from different sources. Fuel N was obtained from a Navy fuel depot and was a conventional MIL-F-16884 Naval Distillate Fuel (NDF). Fuel A consisted of 70 parts by volume of a good quality, aged NDF, and 30 parts by volume of an aged light cycle oil (LCO). The two stocks were supplied separately by NRL and blended before we used them. Fuel B, an Army diesel fuel conforming to Federal Specification VV-F-800 for Fuel Oil, Diesel, was obtained by NRL from an Army base in the continental United States. Some properties of these three fuels are shown in Table 1.

Various types of analyses were conducted on the fuels. Fuel N consisted of about 75% saturates, 2% olefins, and 23% aromatics. Using HPLC techniques, NRL found that Fuel A consisted of about 67% saturates, 21% monocyclic aromatics, and 12% dicyclic and polycyclic aromatics. The composition of Fuel B fell between the other two fuels; it consisted of about 71% saturates, 19% monocyclic aromatics, and 9% dicyclic and polycyclic aromatics.

Table 1. Selected properties of three test fuels.

Property	Fuel N	Fuel A	Fuel B
Gravity, °API, 15.6°C	39.0	31.1	35.0
Viscosity, cSt, 40°C	3.4*	NA**	2.3
Color (ASTM)	NA	L3.5	2.5
Flash Point, °C	80	>60	77
Pour Point, °C	NA	NA	-31
Cloud Point, °C	NA	NA	-21
Distillation, °C			
50% Point	286	276	256
90% Point	340	339	302
End Point	366	360	330
Copper Strip at 100°C	No. 1b	NA	No. 1
Carbon Residue (10% bottom), %	0.09	NA	0.05
Sulfur, % (wt)	0.52	NA	0.40
Ash, % (wt)	NA	NA	0.003
Acid Number, mg KOH/g	0.02	NA	0.02
Accelerated Stability, mg/100 mL	3.9	2.4	3.1
* Measured as 3.5 cSt at 38°C.                      ** NA - Not available.			

#### DESCRIPTION OF PROCEDURES

##### OVERVIEW

Five variables expected to affect the chemistry of the instability reactions were evaluated in a series of D2774-type tests in which the level of one of the variables was changed. The five variables were:

1. The oxygen concentration in the gas contacting the fuel in the oxidation cell.
2. The acidity level in the fuel.
3. Metals and metallic compounds in contact with the fuel in the oxidation cell.
4. The concentration of soluble copper in the fuel.
5. The level of ultraviolet radiation to which the fuel was exposed prior to temperature and oxygen stressing.

Generally, we followed the ASTM D2274 procedure, although we altered specific aspects such as the substitution of nitrogen or air for the oxygen designated in D2274.<sup>\*</sup> Controls were run with both the filterable insolubles and the adherent insolubles determinations, and experimental results were corrected on the basis of the blank values. Finally, we used a NRL cleaning procedure using detergent and solvents rather than chromic acid. All tests were run in duplicate.

#### EFFECT OF OXYGEN

Tests were conducted using oxygen, air, and nitrogen to obtain 100%, 21%, and 0% oxygen concentrations in the gas. Gas flow rates to each cell were set to levels of 0, 1.5, 3.0 and 4.5 L/hr. The bath temperature was held at 95°C, and the stress period was 16 hr as specified in ASTM D2274. One operator tested Fuels A and B; Fuel N was tested earlier by a second operator. Standard D2274 procedures were used following the stress period to obtain filterable insolubles, adherent insolubles, and total insolubles.

#### EFFECT OF ACIDITY

Poor rinsing of chromic acid cleaning solution from the oxidation cells was thought to be one possible reason why different operators and laboratories obtained different results. We evaluated the hypothesis by placing 0, 1, 2, and 4 drops of concentrated sulfuric acid/NOCHROMIX<sup>™</sup> cleaning solution in an oxidation cell and running the D2274 test.

#### EFFECT OF METALS

We used 35 mg of ferric oxide ( $\text{Fe}_2\text{O}_3$ ) to simulate rust, a copper strip such as that used in ASTM D130 (Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test), and a dual copper-iron coil such as

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<sup>\*</sup>NOCHROMIX is a trade name of Godax Laboratories.

that used in ASTM D943 (Test Method for Oxidation Characteristics of Inhibited Mineral Oils) to evaluate the effect of a fuel contacting metal cans during shipment and storage. The 35 mg that represented ferric oxide was subtracted from the filterable insolubles and from the total insolubles to obtain only the values produced in the test. This study was run on Fuel N also.

#### EFFECT OF COPPER

The effect of any copper that may have dissolved in the fuel was evaluated by blending cupric acetylacetonate into 350 mL of fuel to yield concentrations of that compound of 1, 10, 100 and 500 mg/L. The resultant blends were subjected to standard ASTM D2274 tests. Only a single determination was made for each concentration in these tests, and only Fuel N was used.

#### EFFECT OF RADIATION

Four tests were run in duplicate. A filtered fuel sample was first sparged with air, in three of the tests. In the fourth test, a filtered fuel sample was first sparged with nitrogen. Of the three air-sparged samples, one was left unirradiated, one was radiated with ultraviolet light from a lamp approximately a foot from the oxidation cell containing the fuel for a period of 1 hr, and one was radiated for 2 hr. The nitrogen-sparged fuel was radiated for 2 hr. Then, the fuel samples were subjected to standard ASTM D2274 stress conditions and insolubles determined. The results of another test conducted at about the same time provided an indication of D2274 results when Fuel N was not first air-sparged and not exposed to intentional ultraviolet radiation.

## DISCUSSION OF RESULTS

### GENERAL INFORMATION

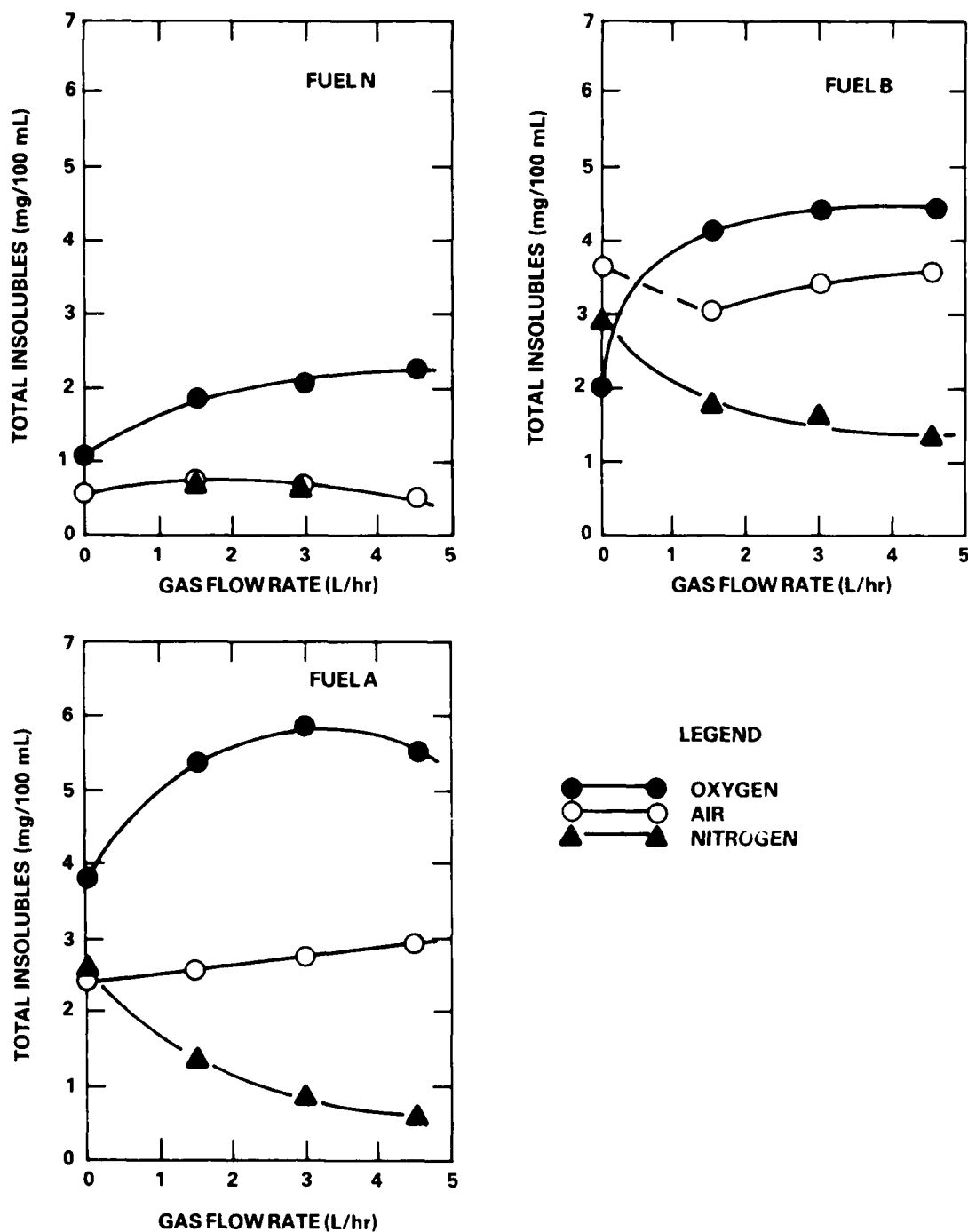
The results are averages of duplicate determinations except where indicated. In general, the discussion will be limited to the effect of the specified variables on the total insolubles formed in the fuels, because the breakdown between filterable and adherent insolubles depends on the surface effects of the apparatus and other undefined factors.

### OXYGEN CONCENTRATION EFFECT

The results of the study of oxygen concentration effects are shown in Figures 1 and 2, which are based on data given in Table A.1 of Appendix A.

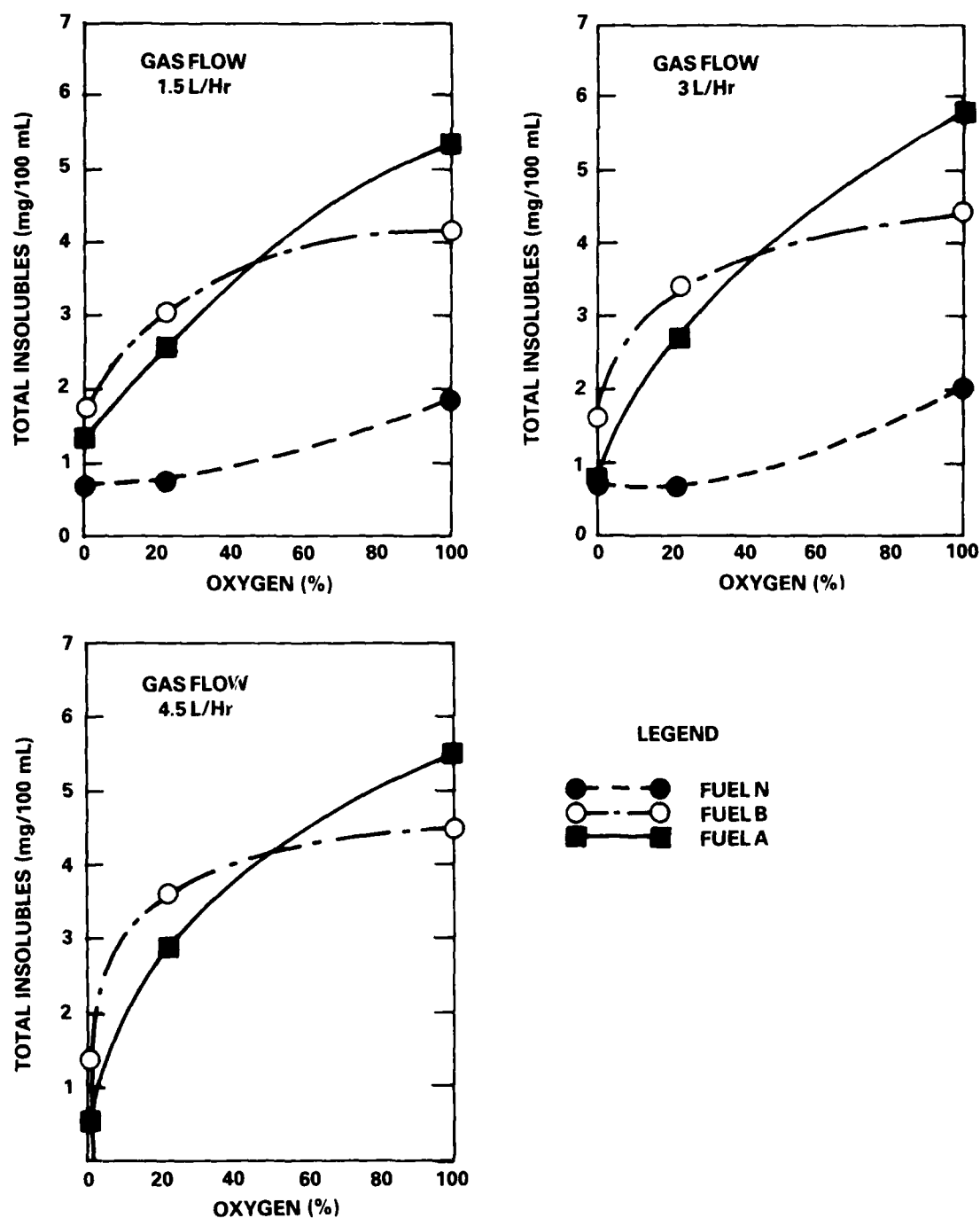
The effects of oxygen concentration on the total insolubles formation are shown for each fuel as a function of gas flow rate in Figure 1. Curves for Fuels A and B are shown for total insolubles produced by oxygen, air, and nitrogen. The figure for Fuel N does not contain a curve for nitrogen, because the air and nitrogen data were almost identical at 1.5 and at 3 L/hr, and these were only two nitrogen flow conditions examined. In each case, the quantity of total insolubles produced is greater when the gas is oxygen than when the gas is air, and in turn, air used as gas produces a greater level of total insolubles than nitrogen. This sequence is expected from the theoretical considerations.

We also expect from theoretical considerations that the three curves for each fuel should coincide at zero gas flow. Examination of Figure 1 shows that the curves tend to approach each other at zero flow. Differences may result from different levels of absorbed oxygen that result from different atmospheric pressures, slightly different fuel ages at the time of the test, or different levels of precursors (e.g., hydroperoxides), in the fuel samples. The possibility of such differences is supported by the zero-flow result obtained with Fuel B when using air.



Note: Plots of total insolubles versus gas flow rate with oxygen, air, and nitrogen as parameters.

Fig. 1. Comparison of the effect of using air or nitrogen in place of oxygen in a D2274 type test on each of three fuels.



Note: Plots of percent oxygen versus total insolubles with fuel as a parameter at three different gas flow rates.

Fig. 2. Effect of the percentage of oxygen in gas used in D2274 type tests on the formation of total insolubles in three fuels.

Relatively smooth curves are obtained in all other cases, but here the zero-flow result departs from the smooth curve.

The nitrogen curves obtained with Fuels A and B are particularly interesting. While increasing the flow of either air or oxygen results in an increase in total insolubles, increasing the flow of nitrogen decreases the formation. We postulate that the flow of nitrogen purges absorbed oxygen from the fuel, providing a lower level of oxygen for the reactions. The greater the flow of nitrogen, the quicker is the purge. However, the curves appear to approach an asymptotic state. There probably are always hydroperoxides in the fuel that are precursors to the instability reaction. These precursors are not volatile enough to be removed by simple purging.

The data are shown in a different manner in Figure 2, where the total insolubles are plotted as functions of the oxygen concentration with the different fuels as parameters. Each of the individual figures relates to a single level of gas flow, 1.5, 3.0, or 4.5 L/hr. It is apparent that compressed air cannot be used for oxygen in the D2274 procedure. Yet, the use of air was reported in a survey of laboratory practices.

#### ACIDITY EFFECT

Figure 3 and Table A.2 show the effects of small quantities of sulfuric acid/NOCHROMIX cleaning solution on the insolubles formed in Fuel N during a standard D2274 determination (16 hr at 95°C).

Figure 3 shows that an increase in the acidity of the system results in an increase in the amount of insolubles formed. Although Figure 3 indicates that this effect may be nonlinear, a linear regression curve fits the data with a correlation coefficient from 0.96 to 0.98 for the three insolubles (adherent, filterable, and total insolubles).

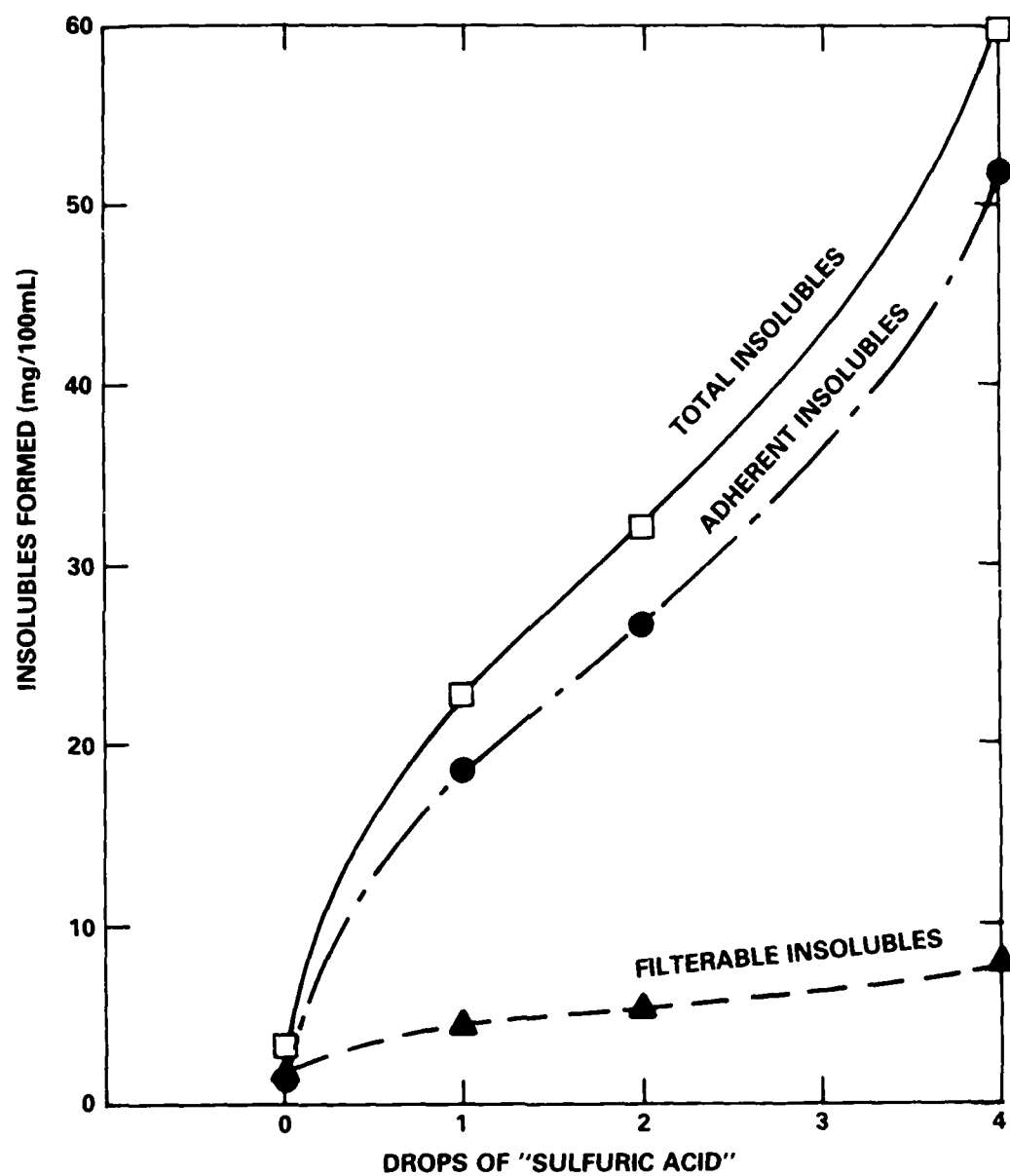


Fig. 3. The effect of small quantities of "sulfuric acid" on the formation of filterable, adherent, and total insolubles in Fuel N.

In all three cases, the confidence level that there is a correlation is in excess of 99%. The three linear equations resulting from the regression analyses, and their corresponding correlation coefficients are:

$$\text{Adherent Insolubles} = 3.22 + 12.20 (\text{No. of drops}) \quad (r = 0.9770)$$

$$\text{Filterable Insolubles} = 2.30 + 1.456 (\text{No. of drops}) \quad (r = 0.9568)$$

$$\text{Total Insolubles} = 5.52 + 13.66 (\text{No. of drops}) \quad (r = 0.9816)$$

Figure 3 clearly shows that the adherent insolubles are the major contributors to the total insolubles in the presence of added "sulfuric acid". In contrast, filterable insolubles predominate in many fuel systems. Because our study was limited to "sulfuric acid", it is not clear whether it was this acid specifically or acidity of the hydronium ion in general that created the reversal in the roles of the adherent and the filterable insolubles.

The results are not surprising as the effect of acidity is supported by other studies reported in the literature, as noted above in the section on Theoretical Background. The important conclusion relative to the D2274 procedure is that it is critical to remove an acidic cleaning agent from the oxidation cells and other glassware.

#### EFFECT OF SELECTED METALS AND METAL COMPOUNDS

These tests were run on a single fuel, Fuel N. The data from this study are shown in Table A.3 and in the form of a bar chart in Figure 4.

An iron oxide (ferric oxide) was added to the base fuel to simulate the effect of rust in a fuel on the formation of insolubles. The quantity of filterable insolubles removed from the fuel at the end of the standard D2274 test then was corrected for the amount of iron oxide that was added to the fuel at the start of the test.

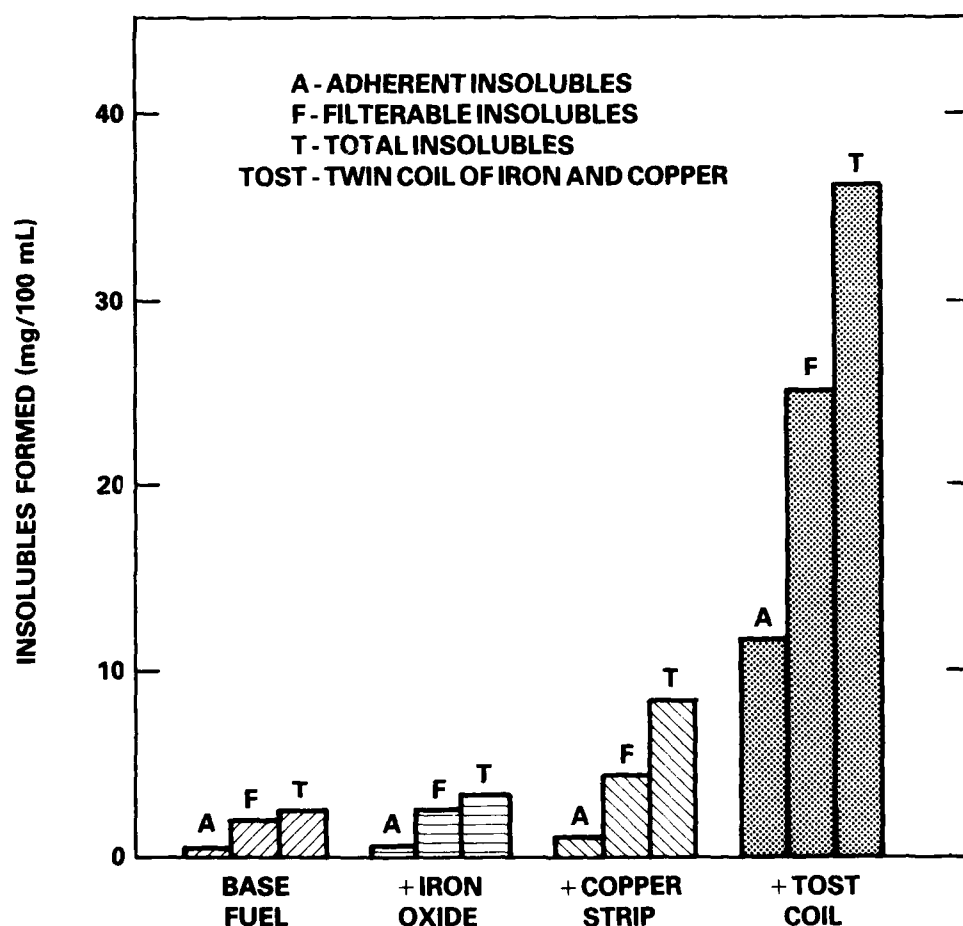


Fig. 4. A comparison of adherent, filterable, and total insolubles formed in fuels when in contact with iron oxide, a strip of copper, and a twin coil of iron and copper, with the formation of the same insolubles in a base fuel that does not contact metals or metal compounds.

Although the results from the fuel containing iron oxide appear to be higher than those from the neat fuel, differences were not statistically significant. The confidence level for the adherent, filterable, and total insolubles was less than 95%; i.e., the differences were due to chance alone. We can conclude that rust had no effect on the stability of Fuel N.

As expected, there were greater effects when a copper strip was left in the fuel during the stress period of the D2274 test. For example, the total insolubles increased to 8 mg/100 mL from the base fuel value of 2.2 mg/100 mL. This was found to be a highly significant increase (>99.5% confidence level). Similarly, the change in the adherent insolubles was found to be significant (>97.5% confidence level), and the change in the filterable insolubles was found to be highly significant (>99.9% confidence level).

The presence of a twin coil of iron and copper (TOST) (ASTM D943) caused the greatest change in the amounts of insolubles formed and these changes were found to be highly significant. Total insolubles increased to 36.6 from the 2.2 mg/100 mL obtained with the neat fuel. Similarly, adherent insolubles increased from 0.24 mg/100 mL in the neat fuel to 11.6 mg/100 mL in the fuel with the TOST coil; filterable insolubles increased from 2 to 25 mg/100 mL. The presence of copper and iron in the coil magnified the effects of either metal alone, because of their electrochemical potentials.

Based on these experiments, we recommend that the fuel sample not be shipped or stored in an unlined metallic container prior to stability tests. The presence of copper, particularly in conjunction with dissimilar metals, should be avoided especially because the combination will produce higher levels of insolubles than copper alone.

## EFFECT OF CONCENTRATION OF SOLUBLE COPPER

We have seen above that metallic copper can accelerate the formation of insolubles in a fuel. It has been postulated that copper dissolved in the fuel is the critical factor, and this too has been studied. The results are shown in Table A.4 and Figure 5.

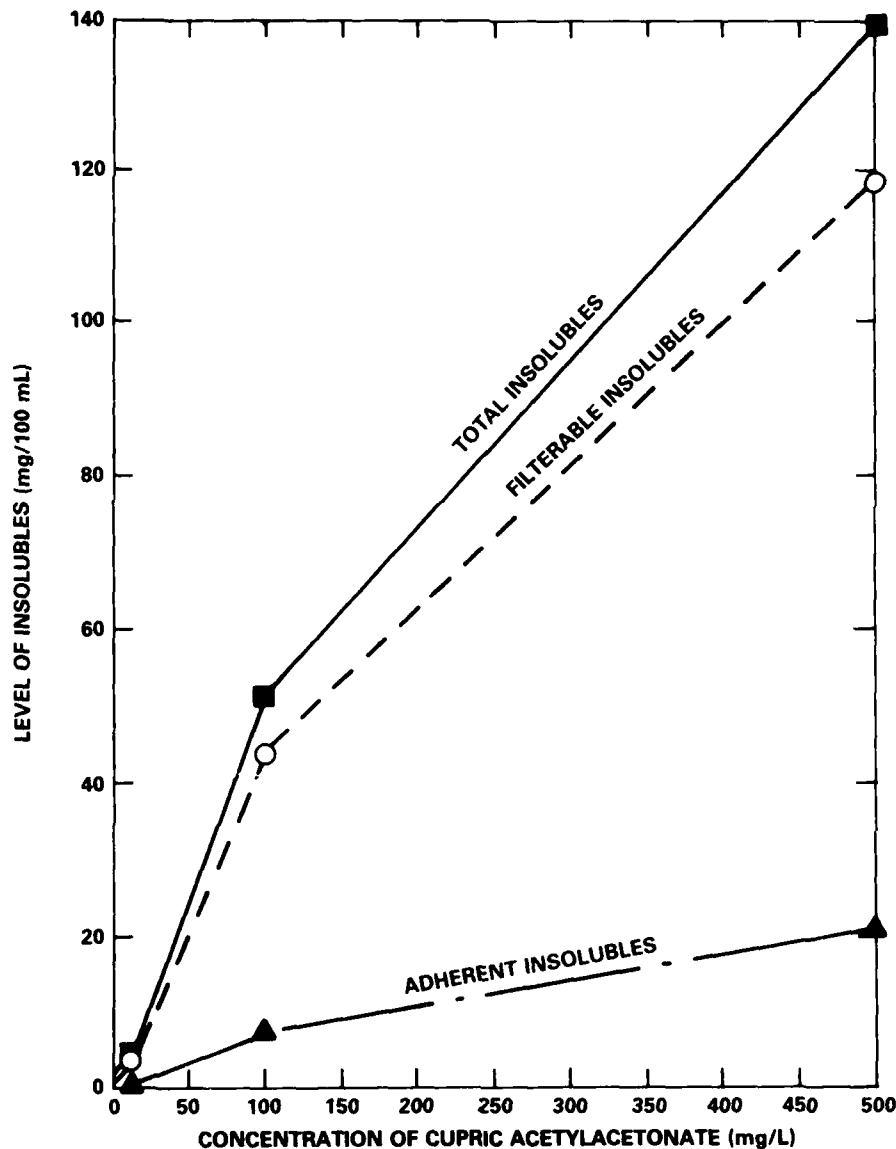


Fig. 5. The effect of the concentration of soluble copper (expressed as milligrams of cupric acetylacetonate per liter of Fuel N) on the formation of adherent, filterable, and total insolubles in a D2274 test of the fuel stability.

Figure 5 shows that both adherent and filterable insolubles, and hence total insolubles, increase with the concentration of cupric acetyl acetate. This is consistent with the reported findings of Daniel.<sup>27</sup> We can develop several regression equations that relate the insolubles to the concentration of copper (expressed as mg/L of cupric acetyl acetate) with excellent correlation coefficients. Several equations for the total insolubles and the correlation coefficient of each are:

$$1/\text{Total Insolubles} = 0.46 + 0.0004 (\text{Cu Conc}) - 0.25 \log (\text{Cu Conc}) \quad (r = 0.9980)$$

$$\text{Total Insolubles} = -1.92 + 0.21(\text{Cu Conc}) + 13.1 (\log \text{Cu Conc}) \quad (r = 0.9954)$$

$$\text{Total Insolubles} = 8.48 + 0.27 (\text{Cu Conc}) \quad (r = 0.9861)$$

$$\log \text{Total Insolubles} = 0.21 + 0.71 \log (\text{Cu Conc}) \quad (r = 0.9842)$$

There is a real causal relationship between the amount of soluble copper in Fuel N and the amount of insolubles formed in that fuel during a standard D2274 test. However, the exact nature of that relationship is not defined by the present study.

#### EFFECT OF ULTRAVIOLET RADIATION

The results of studies of ultraviolet radiation, with and without initial air sparging, are shown in Table A.5 and Figure 6.

In Figure 6, consider only the total insolubles (marked with a "T"). We found significant differences between the base case fuel and all other fuel treatment conditions. Ultraviolet radiation of air-sparged fuel for 1 hr produced a highly significant (confidence level >99.9% ) increase in total insolubles; 2 hr produced an even greater increase. Two hours of ultraviolet radiation without air sparging, but with nitrogen sparging, produced less of an increase than 1 hr with air sparging, but the increase was still statistically significant. Thus, we recommend that an operator never expose a fuel sample to sunlight or other source of ultraviolet radiation prior to, or during, a D2274 test.

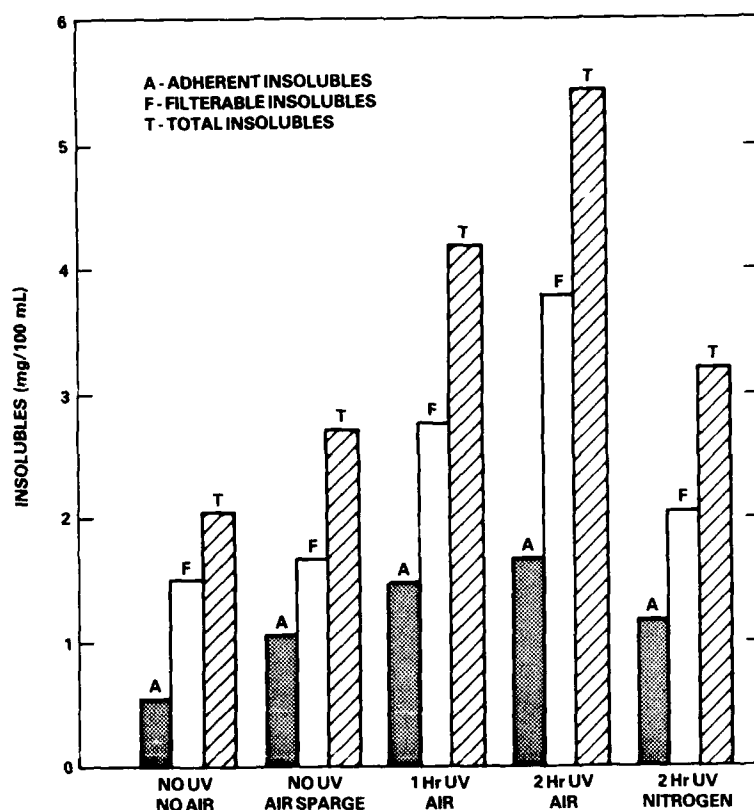


Fig. 6. A comparison of the effect of different levels of ultraviolet radiation and of air-sparging prior to stressing on the formation of adherent, filterable, and total insolubles in ASTM D2274 type tests of Fuel N.

It is interesting to compare the results obtained on a base fuel that was not first air-sparged and the results obtained with the same base fuel when it is air-sparged prior to D2274 testing. There is a highly significant difference in the amount of total insolubles formed in the two cases. Air-sparging results in an increased quantity of insolubles. With reference to the D2274 procedure, this observation implies that different sample histories could explain part of the poor reproducibility of results among laboratories. If one sample has been shaken more than another, either in transportation or by an analyst in preparation for drawing a subsample for the test, a different result could occur due to the different amounts of air beaten into the sample by the shaking.

Consequently, we recommend that undue agitation be avoided in the sampling and shipping of a fuel; similarly, analysts attempting to obtain a representative subsample should not beat air into the fuel.

#### CONCLUSIONS AND RECOMMENDATIONS

If operators evaluating the stability of a mid-distillate fuel by the ASTM D2274 procedure are to obtain the same results (levels of insolubles), air cannot be substituted for oxygen during the test. Lower levels of adherent, filterable, and total insolubles are obtained when air is used in place of oxygen.

Any residue from an acid cleaner used to prepare the oxidation cells and associated glassware for the stressing step of ASTM D2274, must be removed completely. Otherwise, it is certain that higher levels of the various types of insolubles will be obtained relative to the levels obtained with acid-free glassware.

If a mid-distillate fuel is to be tested for inherent stability by ASTM D2274, the fuel sample must never be shipped or stored in unlined metallic cans. Copper, particularly in conjunction with dissimilar metals, should be especially avoided because it will produce higher levels of insolubles in the test.

Soluble copper is a known oxidation catalyst and yields quantities of insolubles in the ASTM D2274 test method that are a function of the copper concentration.

The level of total insolubles formed during D2274 testing of a fuel increased with exposure to ultraviolet light; the longer the exposure, the more the quantity of insolubles obtained. Consequently, a fuel sample should not be exposed to sunlight or other sources of ultraviolet radiation prior to or during the test.

Air-sparging a fuel prior to the D2274 stability test yielded higher levels of insolubles. Agitation and incidental aeration of a fuel should be avoided in the sampling and shipping process, and operators should avoid undue agitation when

obtaining a subsample to conduct the D2274 test. Unavoidable differences in agitation during shipment to laboratories may explain part of the differences among laboratories in round-robin interlaboratory tests of ASTM D2274.

#### ACKNOWLEDGMENTS

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APPENDIX A  
TABLES OF DATA

Table A.1. Average levels of total insolubles obtained with three fuels at several gas flow rates and with several different gases.

Gas Flow Rate (L/hr)	Fuel N	Fuel B	Fuel A
<u>Oxygen</u>			
0	1.10	2.05	3.78
1.5	1.87	4.18	5.34
3.0	2.06	4.48	5.86
4.5	2.24	4.51	5.49
<u>Air (21% Oxygen)</u>			
0	0.57	3.64	2.40
1.5	0.74	3.03	2.56
3.0	0.68	3.46	2.72
4.5	0.50	3.63	2.87
<u>Nitrogen (0% Oxygen)</u>			
0	NA	2.86	2.52
1.5	0.71	1.76	1.35
3.0	0.71	1.63	0.83
4.5	NA	1.36	0.55
NA = Not available			
Note: All values are expressed as mg/100 mL of fuel.			

Table A.2. Effect of small quantities of sulfuric acid plus NOCHROMIX mixture on the formation of insolubles in Fuel N.

No. of Drops of Acid	Insolubles Values* (average + standard deviation) (mg/100 mL of fuel)		
	Filterable	Adherent	Total
0	1.76 ± 0.01	1.48 ± 0.10	3.24 ± 0.09
1	4.31 ± 0.18	18.48 ± 1.62	22.78 ± 1.44
2	5.46 ± 1.15	26.55 ± 1.13	32.01 ± 2.28
4	7.86 ± 0.80	51.82 ± 9.64	59.68 ± 8.85
*Results are averages of duplicate determinations.			

Table A.3. Effect of selected metals and metal compounds on the formation of D2274 insolubles in Fuel N.

	Insolubles Values (mg/100 mL of fuel)											
	Filterable				Adherent				Total			
	First	Second	Avg	Std Dev	First	Second	Avg	Std Dev	First	Second	Avg	Std Dev
Fuel N (Base)	2.00	1.94	1.97	0.04	0.46	0.03	0.24	0.30	2.46	1.97	2.22	0.35
Ferric Oxide*	2.74	2.29	2.52	0.32	0.66	0.46	0.56	0.14	3.39	2.75	3.07	0.45
Copper Strip	7.06	6.63	6.84	0.30	1.17	1.20	1.18	0.02	8.23	7.83	8.03	0.28
TOST Coil	27.1	22.8	25.0	3.0	11.9	11.4	11.6	0.4	39.0	34.2	36.6	3.4
*35 mg of ferric oxide (Fe <sub>2</sub> O <sub>3</sub> ) was added to the 350-mg sample of fuel in each D2274 test. This weight was subtracted from the weight of the material collected on the filter paper in the procedure to determine filterable insolubles, to obtain the corrected value of "filterable insolubles" and hence of "total insolubles".												

Table A.4. Effect of the concentration of soluble copper (expressed as mg of cupric acetylacetonate per liter of Fuel N) on the formation of insolubles in the standard D2274 test procedure.

Concentration (mg/L)	Insolubles Values* (mg/100 mL of fuel)		
	Filterable	Adherent	Total
1	1.63	0.49	2.12
10	4.05	0.98	5.03
100	43.73	7.32	51.05
500	118.5	20.9	139.4
*Values are the results of single determinations.			

Table A.5 Effect of ultraviolet radiation on insolubles formed in D2274 tests on Fuel N.

Test Condition	Insolubles Values (mg/100 mL of fuel)											
	Filterable				Adherent				Total			
	First	Second	Avg	Std Dev	First	Second	Avg	Std Dev	First	Second	Avg	Std Dev
No Treatment	1.51	1.49	1.50	0.01	0.63	0.49	0.56	0.10	2.14	1.98	2.06	0.11
Air-Sparged	1.67	1.63	1.65	0.03	1.00	1.11	1.06	0.08	2.67	2.74	2.70	0.05
Air-Sparged, 1 hr UV	2.80	2.66	2.73	0.10	1.43	1.49	1.46	0.04	4.23	4.15	4.19	0.06
Air-Sparged, 2 hr UV	NA	3.83	NA	NA	1.71	1.57	1.64	0.10	NA	5.40	NA	NA
Nitrogen-Sparged, 2 hr UV	2.06	2.03	2.04	0.02	1.17	1.11	1.14	0.04	3.23	3.14	3.18	0.06
NA - Not available.												

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